

Microstructure-Property Relationships in Concrete: From Nanometers to Centimeters

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Synopsis: Theoretical understanding of how the properties and performance of cement-based materials relate to microstructure is complicated by the large range of relevant size scales. Processes occurring in the nanometer-sized gel pores ultimately affect the performance of these materials at the structural level of meters and larger. One approach to alleviating this complication is the development of a suite of models, consisting of individual digital-image-based structural models for the calcium silicate hydrate gel at the nanometer level, the hydrated cement paste at the micrometer level, and a mortar or concrete at the millimeter to meter level. Computations performed at one level provide input properties to be used in simulations of performance at the next higher level. This methodology is demonstrated for the property of ionic diffusivity in saturated concrete. In addition, the ideas of percolation theory are shown to unify microstructure and many physical phenomena at various length scales in concrete.

key words:

Concrete, models, percolation, microstructure, cement paste, mortar, multi-scale, diffusivity, electrical conductivity

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INTRODUCTION

Predicting the performance of concrete is made difficult by the complexity of the material, which has a complex microstructure [1] and exhibits composite behavior over many length scales [2]. At the scale of millimeters, one can view the concrete as a composite of aggregates and air voids embedded in a continuous cement paste matrix. Even here, however, one still needs to account for the difference in cement paste microstructure and properties in the interfacial zones surrounding each inclusion [3, 4, 5, 6]. At the scale of micrometers, the cement paste is a composite of unhydrated cement particles, hydration products (crystalline and amorphous), and capillary porosity. Finally, the major hydration product of calcium silicate cements, calcium silicate hydrate (C-S-H) gel, is itself a porous material, being a composite of nanometer-sized "particles" and pores. Fig. 1 shows real concrete at many length scales, from that of meters in an actual building, to centimeters in concrete, then to micrometers in cement paste, all the way down to nanometers in a transmission electron micrograph of the calcium silicate hydrate gel.

A better theoretical understanding of the physical processes occurring at each of these scales and how they interact with other scales is necessary to increase the predictability of the performance of concrete [2, 7]. While this large scale range cannot be easily incorporated into a single model for concrete microstructure, it is possible to develop an integrated model in which information gained at one scale is used in computing characteristics at the next higher scale [2, 3, 8, 9], as is demonstrated in this paper. In particular, the models and necessary theoretical ideas are in place for the understanding

of concrete conductivity/diffusivity over all the relevant length scales. This case will be studied in some detail below. In general, this paper focuses on transport properties because of their importance to material degradation and service life.

COMPUTER MODELLING TECHNIQUES

The microstructure of concrete is too complex and random to allow for the development of exact analytical formulas that describe how the properties are related to the microstructure. The only real alternative to empirical formulas is to use computer models to describe microstructure and predict properties. However, a single model that can adequately describe the complexities of the C-S-H nanostructure simultaneously with the random arrangement of aggregate in concrete is far beyond the capabilities of present day computers, and also for the foreseeable future. A different approach must be used: models that are formulated for a given length scale, but that can interact across length scales.

At each length scale of interest, a method for generating appropriate representative three-dimensional microstructures must be chosen. Computational techniques are then employed to compute the physical properties (diffusivity, elastic moduli, etc.) of these composite microstructures. It should be noted that application of these property computation techniques, to be described below, is not limited to model microstructures, as they can be equally applied to 3-D microstructural representations of real materials obtained by tomographic [10] or microscopic [11] techniques. In this paper, we restrict ourselves to models, and begin at the smallest length scale of nanometers.

At the scale of nanometers, in the study described here, the C-S-H gel is modelled as a two-level structure of partially overlapping spherical particles [7]. At the macro level, the larger 40 nm spherical agglomerates shown in the top right image of Fig. 2 are each composed of smaller 5 nm diameter micro level particles, as shown in the top left image of the same figure. The particle sizes and the total porosity at each level have been chosen to be consistent with experimental data from small angle neutron scattering [12] and sorption measurements [13]. The models are generated in continuum space (in a three-dimensional cube with periodic boundaries) and subsequently digitized into a 3-D digital image for the evaluation of properties.

At the scale of micrometers, a cellular-automata based computer model is used to model the microstructural development of cement paste during hydration [14]. Three-dimensional versions of this computer model have been developed both for tricalcium silicate (the major component of portland cement) [15] and for portland cement, consisting of tricalcium silicate, dicalcium

the diffusivity of a composite medium made up of various phases, as has been utilized to estimate the diffusivity of a mortar relative to its component cement paste [4, 5].

To utilize these solution techniques, the properties of each phase in a microstructure must be known or assumed. For example, to compute an elastic modulus of a cement paste microstructure, one must know the elastic properties of the unhydrated cement, the calcium hydroxide, and the C-S-H gel. Often, our approach is to utilize properties computed at one scale level of modelling as input into the computation procedures employed at a higher scale. For example, as will be demonstrated in the results, the conductivity/diffusivity computed for the C-S-H gel nanostructure model can be used as an input property into the cement paste microstructure model, so that the conductivity/diffusivity of cement paste can be computed as a function of w/c and α . Likewise, the diffusivity computed for cement paste can be utilized in the model of concrete at the level of millimeters, to compute the diffusivity of a concrete, the quantity of actual interest to a designer or structural engineer.

PERCOLATION CONCEPTS APPLIED TO CONCRETE

Along with the results of computer models, the ideas of percolation theory [21] are very helpful in understanding the important features of random structures. The main concept of percolation theory is the idea of connectivity. Picture some sort of structure being built up inside a box by randomly attaching small pieces to a pre-existing central core. Percolation theory attempts to answer the question: at what volume fraction does the structure span the box? An alternate form of this question, for a random structure that already spans the box, is: if pieces of the structure are removed at random, when will it fall apart? The percolation threshold is defined by the value of the volume fraction right at the point where there is a change of connectivity.

Fig. 3 shows a simple two dimensional example of these ideas. Circular blobs of "paint" are thrown down at random on a clean sheet of paper, and the area fraction covered by the paint is monitored until the paint blobs form a continuous structure. It is found numerically that the paint blobs will become continuous when they cover approximately 68% of the paper [21]. In Fig. 3 the circles have an area fraction of 72% and so form a connected path. Suppose that the sheet is a viscous liquid, and the circles are solid particles. Then at the circle percolation threshold, the viscosity of the "suspension" will diverge and the elastic shear modulus (zero frequency) will first become non-zero. This is an example of the percolation of a structure that is being randomly built up. If we now think of the paper as a conducting sheet, and the paint

silicate, tricalcium aluminate, tetracalcium aluminoferrite, and gypsum [14]. The cement particles are modelled as digitized spheres following a desired size distribution, with computer memory limitations restricting the allowable particle diameter range being from about 1 to about $40\mu\text{m}$. The hydration process is modelled in discrete cycles consisting of steps for random dissolution, diffusion, and precipitation/reaction. Volume stoichiometry is explicitly maintained by creating the appropriate number of hydration product volume units for each volume unit of cement that dissolves and reacts. Three-dimensional digital-image-based microstructures generated using the models can be subsequently analyzed to determine phase connectivity [16] or diffusion coefficients [17] as a function of water-to-cement (w/c) ratio and degree of hydration (α). The middle portion of Fig. 2 shows a typical two-dimensional microstructure (w/c=0.5, α =87%) generated using the tricalcium silicate hydration model. The unhydrated cement particles are white, capillary porosity is black, calcium hydroxide is light grey, and the C-S-H gel is dark grey.

At the scale of millimeters, mortar or concrete is modelled as a continuum of cement paste containing rigid (nonoverlapping) spherical [18] or ellipsoidal [19] aggregate particles following a size distribution corresponding to that of a real mortar or concrete. Each aggregate can be surrounded by an interfacial zone of some specified thickness, as shown in the bottom image of Fig. 2. Here, the aggregates are shown in dark grey, bulk cement paste is black, the interfacial zones are white, and the single rebar is light grey. One can clearly see the modification of the aggregate distribution in the vicinity of the labelled rebar as well as at the top surface of the concrete and near the larger aggregate particles. Additionally, the interfacial zone cement paste is seen to occupy a large fraction of the total cement paste volume. Typically, we model mortar using a sample volume $1\text{ x }1\text{ x }1\text{ cm}^3$, while for concrete, a sample volume of $3\text{ x }3\text{ x }3\text{ cm}^3$ is employed. Aggregate particle diameters typically range from $75\mu\text{m}$ to 19.05 mm ($3/4''$). With this range of particle sizes, a concrete simulation can require as many as 800,000 separate particles. For this reason, supercomputers are often employed for generating these structures. Once again, this continuum structure can be digitized into a 3-D digital image for the computation of properties, or in certain cases, some properties may be directly computed on the continuum structure.

Properties are generally computed using finite difference or finite element techniques [17, 20]. That is, each cubic pixel in the 3-D microstructure is mapped into a node in either a finite element or finite difference analysis. The resultant physical equations are then solved utilizing conjugate gradient or other fast solution techniques to determine the property of interest such as an elastic modulus or diffusivity. For determining diffusivity, the Nernst-Einstein equation is used to determine the diffusivity by solving the equivalent electrical problem for the electrical conductivity of the composite material [17]. Alternatively, random walk simulations may be employed to estimate

blobs as circular holes that are randomly punched out, then the sheet will lose connectivity and its ability to carry an electrical current at a matrix area fraction of 32%. This is an example of the percolation of a structure that is being randomly torn down. Both kinds of percolation processes are of interest, as both are manifested in concrete.

Consider how these ideas apply to concrete, from mixing to final use, first at the cement paste level. Immediately after mixing, the solid phases in a cement paste are discontinuous, or at most loosely connected via flocculation, and so the freshly mixed paste is a viscous liquid. The solid phase is then built up through quasi-random growth of reaction products, and at some point becomes continuous across the sample, mainly due to the formation of C-S-H gel [22]. This percolation threshold is then a rigorous theoretical definition of the set point [14, 23].

Once the cement paste is set, the next percolation threshold of special interest for transport processes is the point at which the capillary pore space loses continuity. Such a percolation threshold can exist, because as hydration products are formed, pieces of the capillary pore space will be trapped and cut off from the main pore network, thus reducing the fraction of the pores that form a connected pathway for transport. As this process continues, the capillary pore space can lose all long-range connectivity, so that "fast" transport of water or ions through the relatively large capillary pore system would end, and "slow" transport would then be regulated by the smaller C-S-H gel pores.

Results from recent computer simulation work illustrate the capillary porosity percolation threshold. Fig. 4(a) shows the "Fraction Connected" of the capillary pore space vs. degree of hydration for several water:cement ratios, as computed by a computer simulation model of cement paste microstructure [17]. The quantity "Fraction Connected" is defined as the volume fraction of capillary pores that make up a connected path through the sample, divided by the total volume fraction of capillary pores. Immediately after mixing, the cement particles are totally isolated, assuming adequate dispersion, and so the connected fraction of the capillary pore space is one. As hydration occurs the connected fraction decreases gradually. If continuity is lost at some critical degree of hydration, the "Fraction Connected" will go to zero. Such a percolation threshold can be seen in all the water:cement ratios plotted, except for 0.6 and 0.7. We have found in the model that water:cement ratios of 0.6 and above always have a continuous (or percolated) capillary pore system. This prediction is in good agreement with experiment [24]. It is clearly seen in Fig. 4(a) that as the water: cement ratio decreases below 0.6, less and less hydration is required to close off the capillary pore system.

In order to unify the previous results, we have re-plotted all the data from Fig. 4(a) in Fig. 4(b) against capillary porosity. All the connectivity data now falls on one curve, and it is clearly seen that there is a common percolation

threshold at a critical value of capillary porosity of about 18%. Even the 0.6 and 0.7 water:cement ratio data fall on this curve, and now it is clear why these pastes always have an open capillary pore space: there is not enough cement present originally to be able to bring the capillary porosity down to the critical value, even after full hydration. The capillary pore space percolation threshold for cement paste will have some sensitivity to cement particle size distribution and degree of dispersion, so that the critical value of capillary porosity for percolation should be considered to be about $20 \pm 5\%$.

The same model also predicts that the initially fragmented C-S-H phase becomes connected at a volume fraction of about 16 – 20%. Cement paste is, in fact, a good example of an "interpenetrating phase composite" [25], with correspondingly complex properties. The C-S-H becomes connected past the set point, as only the combined cement-C-S-H phase needs to be continuous at set, and not the C-S-H phase itself. Recent impedance spectroscopy results on frozen cement paste have shown the validity of this prediction [26] for the C-S-H percolation threshold.

Percolation also is thought to play a critical role at the millimeter level of mortar and concrete. In this case it is the percolation of the interfacial zones between the cement paste and aggregates that plays a critical role in determining the bulk transport properties. The characteristic feature, as far as transport is concerned, seen in the interfacial zone is higher capillary porosity than in the bulk and generally bigger pores as well [1]. These features are typically seen in the cement paste volume that is within 50 micrometers of an aggregate surface [1].

If a concrete were made out of cement paste and zero porosity aggregate, with no interfacial zones present, then the ionic diffusivity and fluid permeability of the concrete would rigorously have to be lower than the corresponding values for the cement paste. For this kind of composite, the bulk values of transport coefficients are always less than a simple volume average of the individual phase properties, due to the random geometry and the nature of the equations that define the various properties, and only decrease as more of the second phase (aggregate) is added [28].

Some recent work shows that the effective transport properties of concrete can increase greatly as more aggregate is added past a critical amount [29]. There is also data showing that concrete can have up to 100 times the water permeability of the cement paste from which it is made [30]. The only possible microstructural explanation of this behavior, besides that of extensive microcracking, is the effect of transport of fluid or ions through the interfacial zones. It is already known that the interfacial zone regions contain pores larger than those in the bulk paste. However, if the interfacial zones do not percolate, then transport properties would be dominated by the bulk cement paste phase.

To study the percolation or connectivity of the interfacial zones in concrete

is not simple, as the geometry of this phase is complex. Fortunately, in the percolation literature there is a model that is almost perfectly suited for this study, the "hard core/soft shell" model [31]. This model starts with a random suspension of "hard" spherical particles, which are "hard" in the sense that they are packed without being allowed to overlap, as in a suspension. Then concentric spherical shells are placed around each particle, where the spherical shells all have the same thickness, and are allowed to freely overlap. The volume fraction of shells required to make the shells percolate, which is when a continuous soft shell pathway first becomes established, is then computed. The mortar/concrete model described above in Section 2 was based on the hard core/soft shell model, with the interfacial zone taken to be equivalent to the soft shell. The fraction of the total shell or interfacial zone volume that forms part of a connected cluster is then computed as a function of the volume fraction of aggregate present.

Results for a mortar are shown in Fig. 5, in which each curve shows the connectivity of the interfacial zones for different choices of interfacial zone thickness. When comparing against portland cement mortar mercury intrusion data [18], it was found that a choice of $20\mu\text{m}$ for the interfacial zone thickness gave the best agreement with the mercury data. The mercury data gave an idea of what the percolation threshold of the interfacial zones was by showing a large increase in large pores intruded at the mercury breakthrough point [18, 32] at a certain aggregate volume fraction.

The width of $20\mu\text{m}$ given by the hard core/soft shell model is an effective width, where this width contains the larger pores that would be important for transport. Fig. 5 also shows that for an aggregate volume fraction of 40% or more and an interfacial zone thickness of at least $20\mu\text{m}$, the interfacial zones will be percolated at least partially, and will be fully percolated for aggregate volume fractions greater than 50%. Most concretes have aggregate volume fractions well above 50%, so that in general, we can conclude that the interfacial zones in usual portland cement concrete are percolated, and so will have an effect on transport properties.

DIFFUSIVITY AND CONDUCTIVITY

We now show how the various microstructure models can give predictions for properties. The overall approach is demonstrated explicitly for the case of computing the relative diffusivity of concrete. The relative diffusivity is defined as the ratio of the diffusivity of ions in a composite medium to their diffusivity in bulk water. Based on the Nernst-Einstein relation, the relative diffusivity (D/D_0) is equivalent to the relative conductivity (σ/σ_0) [17]. The

results of this computation are summarized in Fig. 6, which is referred to in the discussion which follows.

The first step is the computation of the relative diffusivity of the C-S-H gel. Using the electrical analogy and the nanostructural model shown in the upper right of Fig. 2, a value of $1/300$ is computed for the relative diffusivity of the gel. Here, we assume that diffusive transport occurs only in the cluster-level pores and not in the much smaller pores shown in the particle-level model in the upper left of Fig. 2. This is a reasonable assumption, since these smaller, nanometer size pores are on the order of the size of a water molecule and would be virtually inaccessible to many diffusing ions. A further assumption is that this relative diffusivity value is characteristic of all C-S-H gel regardless of cement composition or when during the hydration process the C-S-H is produced.

The second step is to use the value computed for the relative diffusivity of the C-S-H gel in a computation of the relative diffusivity of cement pastes of various w/c ratios and degrees of hydration. A diffusivity value of 1.0 is assigned to the capillary porosity, while the unhydrated cement and calcium hydroxide are assigned diffusivities of 0.0 since they contain no porosity. Again using the electrical analogy, computations performed for a variety of microstructures have resulted in the development of an equation which relates relative diffusivity to the capillary porosity of the cement paste as shown in Fig. 6. Good agreement has been observed in comparing these computed model values to ones measured experimentally both for chloride ion diffusivity [17, 29] and cement paste conductivity [26, 27].

Building on the percolation results given earlier, the dependence of the diffusivity or electrical conductivity of cement paste on pore structure can now be qualitatively outlined. Early in hydration the capillary pore space is fully percolated, and so dominates the transport. As the capillary porosity decreases, the capillary pores become smaller and only partially connected, so for porosities near but above the percolation threshold, pure capillary pore paths have only slightly more influence on flow than the hybrid paths that are made up of isolated capillary pockets linked by C-S-H gel pores. Below the critical capillary porosity, all flow must now go through C-S-H gel pores, but flow will be dominated by paths that contain some isolated capillary pore regions, and are not just made up of pure C-S-H gel pores. If this were not true, then after a certain point, the diffusivity would begin going up with increasing hydration, since more C-S-H and thus more gel pores are being formed. This is not the case in cement paste.

Finally, the relative diffusivity values computed for cement paste can be used as input into a structural model for mortar to determine the effect of aggregates and their surrounding interfacial zones on the diffusivity of the mortar (D_M). At this level, one must select the thickness of the interfacial

zone paste and the value of its diffusivity (D_{IZ}) compared to that of the bulk paste (D_P). Fig. 6 provides equations which approximate the relative diffusivity of a specific model mortar as a function of aggregate content for three ratios of (D_{IZ}) to (D_P) and an interfacial zone thickness of $20\mu m$ [4, 5]. The mortar is considered to be a model mortar in that only four different size aggregates were utilized in generating its structure. However, the computational techniques described in [4] would be equally applicable to a real mortar specimen, although the computational times will increase in proportion to the number of particles in the simulation.

To display the mortar results in more detail, Fig. 7 shows the results of the conductivity computation for a mortar with 55% sand content by volume. The interfacial zone conductivity is varied with respect to the bulk matrix cement paste conductivity, and the overall conductivity is computed. Note that for this aggregate distribution, the value of σ_{IZ}/σ_P had to be above about 8 in order for the overall conductivity to be larger than the original cement paste conductivity. The lines show the results of analytical effective medium theories [4]. Fig. 8 shows how the mortar conductivity changes with aggregate content for different values of σ_{IZ}/σ_P . The lines are the results of various analytical effective medium theories, which do a reasonable qualitative job of describing the data [4]. It is important to note that the size distribution of aggregate and the interfacial zone thickness determine what value of σ_{IZ}/σ_P is required to make the overall mortar conductivity stay above the cement paste value. In general, we expect that in concrete, the value needed is higher than in mortar, and so concrete conductivities will in general tend to be smaller than mortar conductivities, and could possibly be lower than that of the cement paste from which they are made, as has been observed experimentally [33]. In field concrete, the effect of microcracking has the possibility of significantly modifying this picture, however.

CONCLUSIONS

It has been shown that theoretical understanding of the microstructure:transport property relationships of concrete, from the C-S-H gel up to the full composite, can be modelled using multi-scale computer models, with the ideas of percolation theory providing an overall picture of the microstructure-property relationships. By relating microstructure to properties at all relevant size scales, a more complete understanding of the influence of microstructure and the underlying physical processes on the performance of these composite materials can be obtained. For the case of chloride diffusivity (electrical conductivity), a fairly complete set of results has been presented. As the structural modelling and computational capabilities described herein continue to evolve, their use

as a tool in the design of a concrete with desired properties and service life should become a reality.

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NOTATION

Symbols α - degree of hydration

ϕ - porosity

σ - conductivity

c, d - constants in equation to estimate mortar relative diffusivity

D - diffusivity

$H(x)$ - heaviside function = $(1: x \geq 0; 0 \text{ otherwise})$

V - volume fraction

w/c - water to cement ratio

Subscripts Agg - aggregate

0 - bulk solution

IZ - interfacial zone cement paste

M - mortar

P - bulk cement paste

REFERENCES

- [1] Scrivener, K.L., in Materials Science of Concrete I, edited by J.P. Skalny (American Ceramic Society, Westerville, OH, 1989), p. 127.

- [2] Garboczi, E.J., *Materials and Structures* **26**, pp. 191-195 (1993).
- [3] Bentz, D.P., Schlangen, E., and Garboczi, E.J., in *Materials Science of Concrete IV*, edited by J.P. Skalny and S. Mindess (American Ceramic Society, Westerville, OH, 1994).
- [4] Garboczi, E.J., Schwartz, L.M., and Bentz, D.P., "Modelling the Influence of the Interfacial Zone on the Conductivity and Diffusivity of Mortar," *J. of Advanced Cement-Based Mat.*, in press.
- [5] Schwartz, L.M., Garboczi, E.J., and Bentz, D.P., "Interfacial Transport in Porous Media: Application to D.C. Electrical Conductivity of Mortars," submitted to *Phys. Rev. E*.
- [6] Neubauer, C.M., Jennings, H.M., and Garboczi, E.J., "Modelling the Effect of Interfacial Zone Microstructure and Properties on the Elastic Drying Shrinkage of Mortar," submitted to *J. of Advanced Cement-Based Mat.*
- [7] Bentz, D.P., Quenard, D.A., Baroghel-Bouny, V., Garboczi, E.J., and Jennings, H.M., "Modelling Drying Shrinkage of Cement Paste and Mortar: Part 1. Structural Models from Nanometers to Millimeters," *Mat. and Struc.*, in press.
- [8] Jennings, H.M., and Xi, Y., in *Creep and Shrinkage of Concrete*, edited by Z.P. Bazant and I. Carol (E & F Spon, London, 1993), p. 85.
- [9] Huet, C., in *Micromechanics of Concrete and Cementitious Composites*, edited by C. Huet (Presses Polytechniques et Universitaires Romandes, Lausanne, 1993), p. 117.
- [10] Bentz, D.P., Martys, N.S., Stutzman, P.E., Levenson, M.S., Garboczi, E.J., Dunsmuir, J., and Schwartz, L.M., "X-Ray Microtomography of an ASTM C109 Mortar Exposed to Sulfate Attack," Materials Research Society Fall, 1994.
- [11] Stutzman, P.E., *Ceramic Trans.* **16**, 237 (1991).
- [12] Allen, A.J., Oberthur, R.C., Pearson, D., Schofield, P., and Wilding, C.R., *Phil. Mag. B* **56** (3), 263 (1987).
- [13] Baroghel-Bouny, V., PhD thesis, L'ecole Nationale des Ponts et Chaussees, Paris, France 1994.
- [14] Bentz, D.P., Coveney, P.V., Garboczi, E.J., Kleyn, M.F., Stutzman, P.E., *Modelling and Sim. in Mat. Sci. and Eng.* **2** (4), 783 (1994).
- [15] Bentz, D.P., and Garboczi, E.J., "Guide to Using HYDRA3D: A Three-Dimensional Digital-Image-Based Cement Microstructure Model," NISTIR **4746**, U.S. Department of Commerce (1992).
- [16] Bentz, D.P., and Garboczi, E.J., *Cem. and Conc. Res.* **21**, 325 (1991).
- [17] Garboczi, E.J., and Bentz, D.P., *J. of Mat. Sci.* **27** 2083 (1992).
- [18] Winslow, D.N., Cohen, M.D., Bentz, D.P., Snyder, K.A., and Garboczi, E.J., *Cem. and Conc. Res.* **24** (1), 25 (1994).
- [19] Bentz, D.P., Hwang, J.T.G., Hagwood, C., Garboczi, E.J., Snyder, K.A., Buenfeld, N., Scrivener, K.L., "Interfacial Zone Percolation in Concrete:

- Effects of Interfacial Zone Thickness and Aggregate Shape," Materials Research Society Fall, 1994.
- [20] Garboczi, E.J., and Day, A. R., "An Algorithm for Computing the Effective Linear Elastic Properties of Heterogeneous Materials: 3-D Results for Composites with Equal Phase Poisson Ratios," submitted to *Physics and Mechanics of Solids*
 - [21] Stauffer, D., Introduction to Percolation Theory (Taylor and Francis, London, 1985).
 - [22] Chen, Y., and Odler, I., "On the Origin of Portland Cement Setting", *Cem. Conc. Res.* 22, 1130-1140 (1992).
 - [23] Boumiz, A., Vernet, C., and Tenoudji, F.C., "Mechanical properties of cement pastes and mortars at early ages. Evolution with time and hydration degree", *J. of Advanced Cement-Based Materials*, in press.
 - [24] Powers, T.C., Copeland, L.E., and Mann, H.M., PCA Bulletin 10 (1959).
 - [25] Clarke, D.R., *J. Am. Ceram. Soc.* 75, p. 739-759 (1992).
 - [26] Olson, R.A., Christensen, B.J., Coverdale, R.T., Ford, S.J., Moss, G.M., Jennings, H.M., Mason, T.O., and Garboczi, E.J., "Microstructural Analysis of Freezing Cement Paste Using Impedance Spectroscopy," submitted to *J. of Mat. Sci.*
 - [27] Christensen, B.J., Mason, T.O., Jennings, H.M., Bentz, D.P., and Garboczi, E.J., "Experimental and computer simulation results for the electrical conductivity of portland cement paste", in Advanced Cementitious Systems: Mechanisms and Properties (Materials Research Society, Pittsburgh, 1992).
 - [28] Hashin, Z., "Analysis of Composite Materials: A Survey", *J. Appl. Mech.* 50, 481-505 (1983).
 - [29] Halamickova, P., Detwiler, R.J., Bentz, D.P., and Garboczi, E.J., "Water Permeability and Chloride Ion Diffusion in Portland Cement Mortars: Relationship to Sand Content and Critical Pore Diameter," *Cem. and Conc. Res.*, in press.
 - [30] Young, J.F., "A Review of the Pore Structure of Cement Paste and Concrete and Its Influence on Permeability", in *Permeability of Concrete*, ed. by D. Whiting and A. Walitt, ACI SP- 108 (American Concrete Institute, Detroit, 1988).
 - [31] Torquato, S., *J. Chem. Phys.* 85, 6248 (1986).
 - [32] Winslow, D.N., and Diamond, S., *ASTM J. of Materials* 5, 564 (1970).
 - [33] Luping, T. and Nilsson, L.O., *ACI Materials J.* 49, 49-53 (1992).